Rearrangement of Allylic Silylsulphonium Ylides. A Synthesis of βγ-Unsaturated Aldehydes

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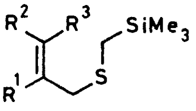
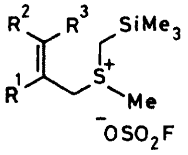
Summary The ylides derived from the reaction of allylic silylmethylsulphonium salts with n-butyl-lithium rearrange to homoallylic α-methylthiosilanes which are precursors to βγ-unsaturated aldehydes.

Silicon can have a pronounced effect on the chemistry of sulphur compounds. For example carbanions co-operatively stabilized by both elements[1] form readily at low temperature and are stable and moderately nucleophilic. Similarly, silicon-activated Pummerer rearrangement of sulphoxides[2] proceeds at room temperature or below to give hydrolytically labile *O*-trimethylsilylhemithioacetals. A combination of these advantageous properties was recently used in a new procedure for nucleophilic formylation.[3,4] We now report a permutation which gives βγ-unsaturated aldehydes.

When the *S*-allylic thiomethylsilane (**1c**) was metallated at 0 °C with n-butyl-lithium in tetrahydrofuran (THF), a [2,3] sigmatropic rearrangement of the resultant carbanion was observed, to give the lithium thiolate (**4c**) which could be alkylated with methyl iodide to give the sulphide (**5c**) in 55% yield accompanied by several minor by-products which were difficult to separate. By contrast, the *S*-allylic *S*-trimethylsilylmethylsulphonium fluorosulphonate salts (**2**), prepared in high yield from the sulphides (**1**)[5] by reaction with methyl fluorosulphonate in CH_2Cl_2 at 0 °C, reacted with n-butyl-lithium in THF at −78 °C to give the ylides derived from selective deprotonation of the carbon bearing silicon and sulphur. The ylides (**3**) underwent a [2,3] sigmatropic rearrangement below −20 °C to give the homoallylic α-methylthiosilanes (**5**) cleanly and in good yield (65—75%). Minor by-products (**6**) and (**7**) (*ca.* 10% each) presumably



(1)



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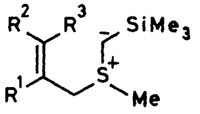

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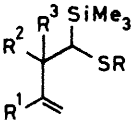
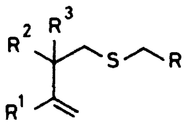
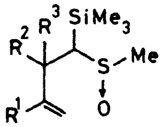


(4) R = Li
(5) R = Me



(6) R = H
(7) R = SiMe₃



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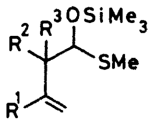

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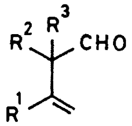

(10)

	R^1	R^2	R^3
a	H	$-[CH_2]_5-$	
b	H	$CH_2CH{=}CMe_2$	Me
c	$-[CH_2]_4-$		H
d	$-[CH_2]_2CMe_2-$		H

arose from rearrangement of alternative ylides generated by deprotonation of the SMe group in the case of (**7**) and desilylation in the case of (**6**).

The rearranged α-methylthiosilanes (**5**) were converted into the aldehydes (**10**) in 40—60% overall yield *via* the sila-Pummerer reaction. Oxidation of (**5**) with 1 mol. equiv. of *m*-chloroperbenzoic acid in CH_2Cl_2 at −40 °C gave the thermally labile sulphoxides (**8**) which had rearranged to the *O*-trimethylsilylhemithioacetals (**9**) after the usual extractive work-up. These were hydrolysed in aqueous THF at 20 °C for 18 h in the presence of 1 mol. equiv. of oxalic acid. It is noteworthy that in the synthesis of γ-cyclocitral (**10d**), the hydrolysis of (**9d**) proceeded without rearrangement of the unstable double bond into conjugation with the carbonyl group.

The present work expands the scope of carbon–carbon bond-forming reactions available to nucleophiles stabilized by sulphur and silicon and provides a useful application of silicon-substituted sulphonium ylides about which little is known.[6]

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[5] Prepared by reaction of the allylic chloride with trimethylsilylmethanethiol in ethanolic sodium ethoxide. The thiol is known: D. C. Noller and H. W. Post, *J. Org. Chem.*, 1952, **17**, 1393.

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